Lithographic engineering of volume plasmons

Vitor R. Manfrinato[a#*], Richard Hobbs[a#], Yujia Yang[a#], Lihua Zhang [b], Dong Su[b],
Sarah A. Goodman[a], Eric A. Stach[b], and Karl K. Berggren[a].
[a] Electrical Engineering and Computer Science Department, MIT, MA, USA
[b] Center for Functional Nanomaterials, Brookhaven National Laboratory, NY, USA
# equal contribution; *electronic mail: vitor@mit.edu

Volume plasmons (VPs) are the bulk analogues of surface plasmons (SPs) and may be defined as collective longitudinal charge-density waves in the bulk of a material. VP resonances lie in the 3-30 eV energy range and have not yet – to our knowledge – been precisely controlled by nanolithography. According to the Drude model, the VP resonance is related to the dielectric function and the complex index of refraction of a material. Therefore, the engineering of VPs permits the control of the optical properties of materials in the 3-30 eV range, enabling new nano-optical devices in the vacuum ultraviolet (VUV). The engineering of VPs is a significant challenge because VPs typically decay on the sub-femtosecond time scale and on the sub-20-nm length scale. Previous results showed that control of VP energy is limited to small (<1 eV) VP energy shifts in chemically synthesized nanostructures[1-3] and thin films.[4] Thus, there is a need to develop a systematic top-down process to fabricate nanostructures that could control VP resonances and take advantage of this newly developed control. Here we present the lithographic fabrication of Al nanodisks with diameter varying from 6 to 20 nm. For each nanodisk we measured the VP and SP resonances using electron energy-loss spectroscopy (EELS).

Figure 1a1 shows an Al nanodisk fabricated by electron-beam lithography (EBL) and lift-off. Figure 1b shows the increase of VP energy by decreasing the nanodisk diameter. Figure 1c shows a significant increase in the full width at half maximum (FWHM) of the VP peak with decreasing nanodisk diameter, indicating a reduced plasmon lifetime. In order to understand these results, we investigated the boundary effect (*begrenzung* effect) by measuring the VP energy and FWHM across a given nanodisk. The VP energy and FHWM are modified near the edge of every nanodisk (Figure 2), in agreement with a previous report.[2] The results shown in Figures 2a and 2b are similar to those in Figures 1b and 1c, respectively. Therefore, we suggest that the increase in VP energy and FHWM with decreasing radius is related to the increased surface-to-volume ratio. Additionally, we obtained significant control of SPs in these nanodisks, and have pushed the SP energy up to 7 eV. Finally, we will show comprehensive numerical and analytical calculations of VPs and SPs in these Al nanostructures.

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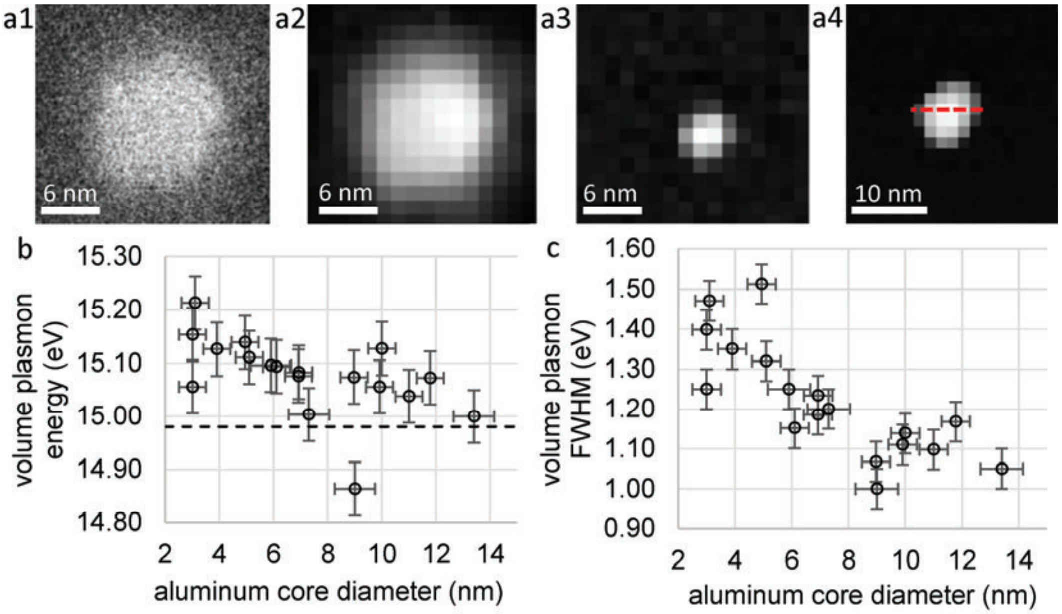

Figure 1. Volume plasmons (VPs) in Al nanodisks with varying diameter. **(a1)** Scanning transmission electron micrograph of a 15-nm-thick Al nanodisk on top of 5-nm-thick SiN_x. **(a2)** High angle annular dark field signal collected during electron energy loss spectroscopy (EELS) acquisition across the entire nanodisk in (a1). Each pixel in (a2) contains one EELS spectrum. **(a3)** Image of the nanodisk core, which consists of pure Al, as opposed to Al oxide that surrounds the nanodisk. The diameter of the nanodisk core was 5.9 nm. The EELS signal was integrated from 13 to 17 eV after background subtraction. The gray scale level in (a3) is proportional to the integral of the VP peak of pure aluminum. **(a4)** Image of a nanodisk core with 7.5 nm diameter. The dashed-red line in (a4) marks a cross section across the diameter of the disk to be analyzed in Figure 2. **(b)** Shows the VP peak energy at the center of the nanodisks as a function of the core diameter of the nanodisks. The dashed line shows the measured VP peak energy for bulk Al. We observed a small increase in the VP energy for smaller nanodisks. **(c)** Shows the VP full width at half maximum (FWHM) of the VP peak as a function of the core diameter of the nanodisks. We observed a significant increase in the VP FWHM for smaller nanodisks.

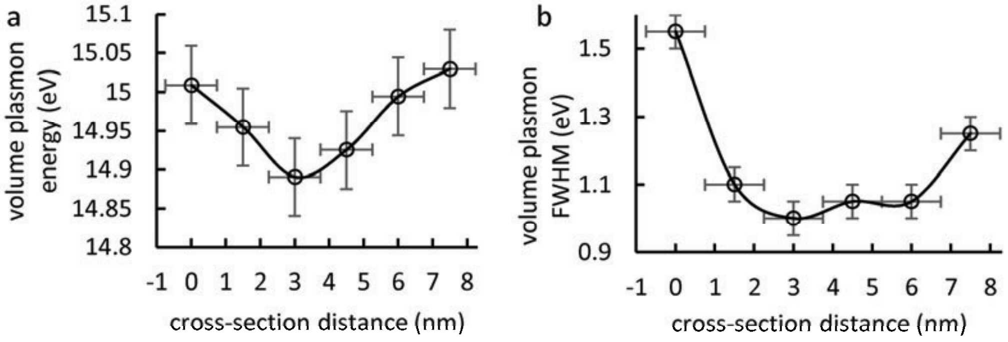

Figure 2. Measurement of the boundary effect. **(a)** Shows the VP peak energy along the cross section marked in Figure 1a4. We observed a small increase in the VP energy at the edges. **(b)** Shows the VP full width at half maximum (FWHM) of the VP peak along the cross section marked in Figure 1a4. We observed a significant increase in the VP FWHM also at the edges. This boundary effect is present in all nanodisks studied.